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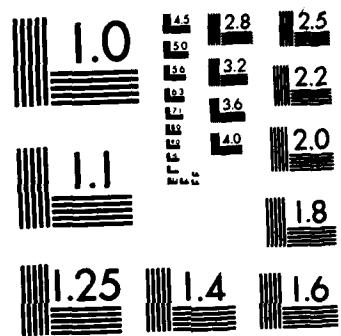
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Reactions from Higher Excited States

by

U. Schmitt and D. M. Burland

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**THE USE OF HOLOGRAPHY TO INVESTIGATE PHOTOCHEMICAL REACTIONS
FROM HIGHER EXCITED STATES. (ACTION SPECTRUM OF THE SECOND-PHOTON
STEP IN THE TWO-PHOTON DISSOCIATION REACTION OF CARBAZOLE)**

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ABSTRACT: A holographic technique has been used to investigate photochemistry that occurs from higher excited triplet states (i.e., T_2 and above). Specifically, the two-photon dissociation of carbazole in poly(methyl methacrylate) films has been investigated. The photochemical action spectrum of the second-photon step is found to be in good agreement with the carbazole triplet-triplet absorption spectrum. This implies that the quantum yield for photodissociation is independent of photon energy in this wavelength region.

1. INTRODUCTION

Recently it has been shown²⁻⁴ that the technique of holography can be used to follow the course of a photochemical reaction in solid samples of optical quality. The photochemistry of camphorquinone,² tetrazine,⁵ and benzophenone,⁶ all in polymer host matrices, has been investigated by this method. In these experiments information about the photochemical processes was obtained by monitoring the temporal growth of holograms as a function of laser intensity.

In this paper we report the action spectrum of the second-photon step in the two-photon dissociation reaction of carbazole. A simple method is described that allowed us to obtain this information using holography. Carbazole was chosen to demonstrate the technique because its photochemistry is reasonably well understood⁷⁻¹⁰ and because two-photon holographic recording has already been demonstrated¹¹ using the photodissociation reaction from its higher triplet state.

Figure 1 shows an energy level diagram for carbazole based on experimental and calculated data.^{12,13} Assuming that the energies of the N-H bond in carbazole and in pyrrole are similar, we estimate the threshold energy for N-H bond rupture to be about 4.3 eV.¹⁴ This value is also included in Fig. 1. Neither the lowest singlet nor the lowest triplet state are energetic enough for carbazole dissociation. Reaction can occur from higher excited singlet¹⁰ or triplet⁷⁻⁹ states, however. When carbazole is dissolved in a polymer film (e.g., poly(methyl methacrylate), PMMA) the photodissociation reaction is accompanied by a change in the index of refraction of the material. This change is due to reactions involving the products of carbazole photodissociation (carbazyl radicals and hydrogen atoms) with the host material. The change in the index of refraction can be utilized to record holograms.

According to theory^{3,4} the efficiency of a photochemical holographic grating depends quadratically on the concentration of photoproducts. The latter is a linear function of the extinction coefficient of the triplet-triplet absorption and of the quantum yield of the photoreaction. Therefore, by measuring hologram growth rates as a function of the wavelength of the holographic laser it should be possible to obtain the action spectrum of the photoreaction.

2. EXPERIMENTAL

2.1 Holographic Technique

Previous holographic experiments on carbazole¹¹ were done in the following way. A spatially uniform concentration profile of carbazole in its lowest triplet state was generated (via intersystem crossing from the lowest excited singlet state) by illumination of the sample with UV light. Simultaneously the sample was irradiated by two mutually coherent laser beams of a wavelength close to the maximum of the triplet-triplet absorption. The interference of these beams gave rise to a spatially periodic excitation of carbazole molecules from their lowest triplet state to higher excited triplet states. Reaction from these higher excited states then produced a spatially periodic change in the index of refraction. The formation of this holographic dielectric grating could be monitored by its diffraction of the laser beams.

In order to get the action spectrum of the second-photon step using this version of the holographic technique, one would have to monitor the temporal growth of the grating for holograms produced at a number of different wavelengths. But changing the wavelength of the laser used to grow the hologram would also require a change in the geometry of the experimental setup in order to keep the fringe spacing and related parameters constant. Considerations like this are especially important when a probe laser is used to monitor the

diffraction efficiency at a fixed wavelength. Since carbazole does not react from its lowest triplet state we found it more convenient to use a slightly different approach.⁵ Operating the holographic laser in the UV, a spatially periodic concentration of carbazole in its lowest triplet state is produced. Spatially uniform irradiation by a second light source (in this case a laser called the boosting laser) in the triplet-triplet absorption band then triggers the photodissociation reaction. The spatial distribution of photoproducts and of changes in the index of refraction reflects the periodic intensity profile of the UV light. Therefore the fringe spacing of the holographic grating is independent of the wavelength of the second photon. The boosting laser changes the hologram growth rate but cannot by itself produce a hologram.

2.2 Sample Preparation

The samples were 0.16 mm thick films of PMMA containing carbazole at a concentration of 5% by weight. They were deposited from a solution of 1.5g PMMA and 75 mg carbazole in 25 ml toluene. Glass rings of 27 mm inner diameter and 4 mm height were glued to common microscope slides. 2.3 ml of the above solution were used to fill this cavity. The solvent was allowed to evaporate slowly over a period of two days. The resulting films were of good optical quality and had absorbances of 0.4 at 351 nm and of 0.2 at 364 nm.

2.3 Apparatus

A diagram of the experimental setup is shown in Fig. 2. Object and reference beams derived from the output of an Ar-ion laser (Coherent Innova 90-5), designated the holographic laser, illuminated a small area of the sample. The laser was fitted with UV optics to produce simultaneous output at 351.1 and 363.8 nm, and it was operated in light control mode at a total power of 40 mW. The angle between the two interfering beams was 2.5°.

(0.04 rad). The same region of the sample was irradiated with the beam of a Kr-ion laser (Spectra-Physics 171-01), designated the boosting laser. Wavelengths of 413.1, 476.2, 530.9, and 647.1 nm from this laser have been used.

A small HeNe laser (Spectra-Physics 145-01) was utilized to monitor the growth of the holograms. The angle of incidence of its beam with respect to the holographic laser beams was adjusted to match the Bragg condition.¹⁵ The intensity of the diffracted light of the HeNe laser was measured by means of a hybrid packaged photodiode/amplifier combination (United Detector Technology UDT Photop 500). The spectral response of this detector was limited by a 632.8 nm (2.8 nm FWHM) interference filter (Melles Griot). To improve the signal to noise ratio further, the HeNe laser beam was chopped, and a lock-in amplifier (Ithaco Dynatrac 391A) was utilized to amplify the output signal of the light.

3. RESULTS AND DISCUSSION

Hologram efficiency (i.e., the ratio of diffracted to incident intensity of the probe laser beam) as a function of time was recorded at four different wavelengths of the gating laser. All measurements were made at room temperature (25°C). The output power of the laser which was chosen so that the holograms grew to their maximum efficiency of about 0.8% in approximately the same time (30-120 min) was 0.08W at 413.1 nm, 0.32W at 476.2 nm, 0.9W at 530.9 nm, and 2.5W at 647.1 nm. As an example Fig. 3 shows the initial part of one of the growth curves of hologram efficiency obtained at 647.1 nm.

Assuming steady state conditions for the concentrations of all the intermediate states involved the kinetic equation for the build-up of the concentration of photoproducts [P] is readily derived:

$$\frac{d[P]}{dt} = (\ln 10/Nhc)^2 [C] \epsilon'(\lambda') \epsilon(\lambda) \lambda' \lambda I' I \phi' \phi(\lambda) \tau . \quad (1)$$

Here $[C]$ is the concentration of ground-state carbazole, ϵ' and ϵ are the extinction coefficients of the singlet-singlet and triplet-triplet absorption, λ' and λ are the wavelengths and I' and I are the intensities used for the excitation of the lowest singlet and triplet states, respectively, ϕ' is the quantum yield of intersystem crossing, $\phi(\lambda)$ is the quantum yield of photodissociation, and τ is the lifetime of the lowest triplet state; N is Avogadro's number, h Planck's constant, and c the speed of light.

When the Bragg condition is satisfied the diffraction efficiency η of a pure phase or index of refraction hologram (in our case only a phase hologram is produced because there is no absorption at the wavelength λ'' of the probe laser) is given by¹⁵

$$\eta = \sin^2(\pi d n' / \lambda'' \cos\theta), \quad (2)$$

where d is the thickness of the sample, θ is the (Bragg) angle of the probe laser beam with respect to a plane parallel to the fringes, and n' is the amplitude of the spatial modulation of the index of refraction and is proportional to $[P]$,⁴

$$n' = \kappa[P]. \quad (3)$$

After substituting n' in Eq. (2) by $[P]$ according to Eq. (3), we combine Eqs. (1) and (2) to yield an expression for the action spectrum of the second step in the photodissociation reaction,

$$\epsilon(\lambda)\phi(\lambda) = \zeta/([C]\lambda I) d/dt(\arcsin\sqrt{\eta})$$

or¹⁶

$$\epsilon(\lambda)\phi(\lambda) = [\zeta/([C]\lambda I)][1/\sqrt{1-\eta} d\sqrt{\eta}/dt], \quad (4)$$

where

$$\zeta = (Nhc/\ln 10)^2 \lambda'' \cos\theta / (\pi d \lambda \epsilon'(\lambda') \lambda' I' \phi' \tau)$$

contains all the parameters that were held constant in our experiments.

The intensity I of the boosting laser beam is the quotient of the output power P and the illuminated area σ which is a linear function of the wavelength λ ,

$$I = P/\sigma = P\lambda^0/\sigma^0\lambda, \quad (5)$$

where σ^0 is the area at wavelength λ^0 .

If we confine ourselves to the initial stage of hologram formation when $[P]$ is small $[C]$ can be considered approximately constant. Further, as long as diffraction efficiencies η are small, $1/\sqrt{1-\eta} \approx 1$ (up to efficiencies of 2% the relative error of this approximation is less than 1%). Substituting Eq. (5) into Eq. (4) and defining a new constant δ by

$$\delta = \xi\sigma^0/(\lambda^0[C]) \quad (6)$$

we finally obtain

$$\epsilon(\lambda)\phi(\lambda) \approx \delta/P \sqrt{\eta}/dt. \quad (7)$$

This equation is identical with the approximation $\eta \approx a(I)t^2$ given in previous papers (cf. Eq. (1) in Ref. 2 and Eq. (28) in Ref. 4) if one defines $a(I) = (\epsilon(\lambda)\phi(\lambda)P/\delta)^2$. From Fig. 3 it can be seen that $d\sqrt{\eta}/dt$ is constant over the initial period of the experiment, indicating that the approximations made in deriving Eq. (7) are valid and that $\epsilon(\lambda)\phi(\lambda)$ is independent of time.

Five recordings were done at each wavelength λ of the boosting laser, and the initial part of the growth curves was fitted to Eq. (7) by plotting $\sqrt{\eta}$ vs. time t . In all cases straight lines were obtained, similar to the one shown in Fig. 3. In Fig. 4 the slopes of these lines divided by the corresponding laser powers are plotted vs. the wavelength of the boosting laser. The error bars indicate the range of dispersion of the data. Since we do not know the numbers for all the parameters that are contained in the constant δ , the greatest

unknown being the factor κ (cf. Eq. (3)), we cannot derive absolute values for the quantity $\epsilon(\lambda)\phi(\lambda)$.

Due to the limited number of wavelengths available from the Kr-ion laser the number of data points along the E/hc axis is small, but nevertheless, the agreement with the triplet-triplet absorption spectrum from Ref. 8 (measured in cyclohexane solution at 25°C) is significant.

Although all carbazole triplet-triplet absorption spectra we have found in the literature^{8,10,12,17-19} are very similar to each other in the region below 550 nm there appears to be some uncertainty as to whether or not there is a weak absorption band near 640 nm. Of the four spectra that show data above 600 nm two do have a band there,^{10,13} the other two^{18,19} do not. It is difficult to obtain reliable data in this region because the carbazyl radical which is formed in the experiments, especially at high intensities of the monitoring light, strongly absorbs in the 550-660 nm interval.^{7,8,20} If the most recent data¹⁰ are correct then our results at 647.1 nm would indicate that the quantum yield ϕ at this wavelength is about one fifth of that at the other ones.

It should be noted that despite the fact that the carbazole triplet also absorbs at the wavelengths of the holographic laser (351.1 and 363.8 nm) no significant hologram growth has been observed when the boosting laser beam was blocked. The output power of the holographic laser was kept sufficiently low to prevent high steady-state concentrations of carbazole triplets. For $\lambda' = \lambda$ and $I' = I$ it can be seen from Eq. (1) that the rate of the photodissociation reaction due to irradiation with the holographic laser alone is proportional to the square of the intensity.

In ethanol solution at 77K biphotonic ionization of carbazole rather than dissociation has been observed by Bagdasar'yan and coworkers.^{18,21} In the 260-344 nm interval the quantum yield of this reaction was found to decrease exponentially with decreasing energy of the second photon, and no photoionization could be detected for wavelengths of 366 nm and 436 nm.¹⁸ Therefore, it is unlikely that photoionization is an important reaction channel in our system under the chosen experimental conditions.

4. CONCLUSION

In conclusion we have demonstrated that the technique of holography can be used to measure the action spectrum of a photoreaction in a rigid medium provided the reaction is accompanied by a change in the index of refraction or in the absorption coefficient²² at the read-out wavelength. For the specific case of carbazole photodissociation treated here, we have shown that the action spectrum very strongly resembles the triplet-triplet absorption spectrum, except perhaps on the long wavelength side where there is some disagreement about the absorption spectrum itself. This means that in the wavelength region investigated, the quantum yield of this reaction is independent of the energy of the second photon.

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16. Recalling that $d/dx (\arcsin u) = 1/\sqrt{1-u^2} du/dx$.
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22. See Refs. 15 and 4 for the more general forms of Eqs. (2) and (3), including absorption.

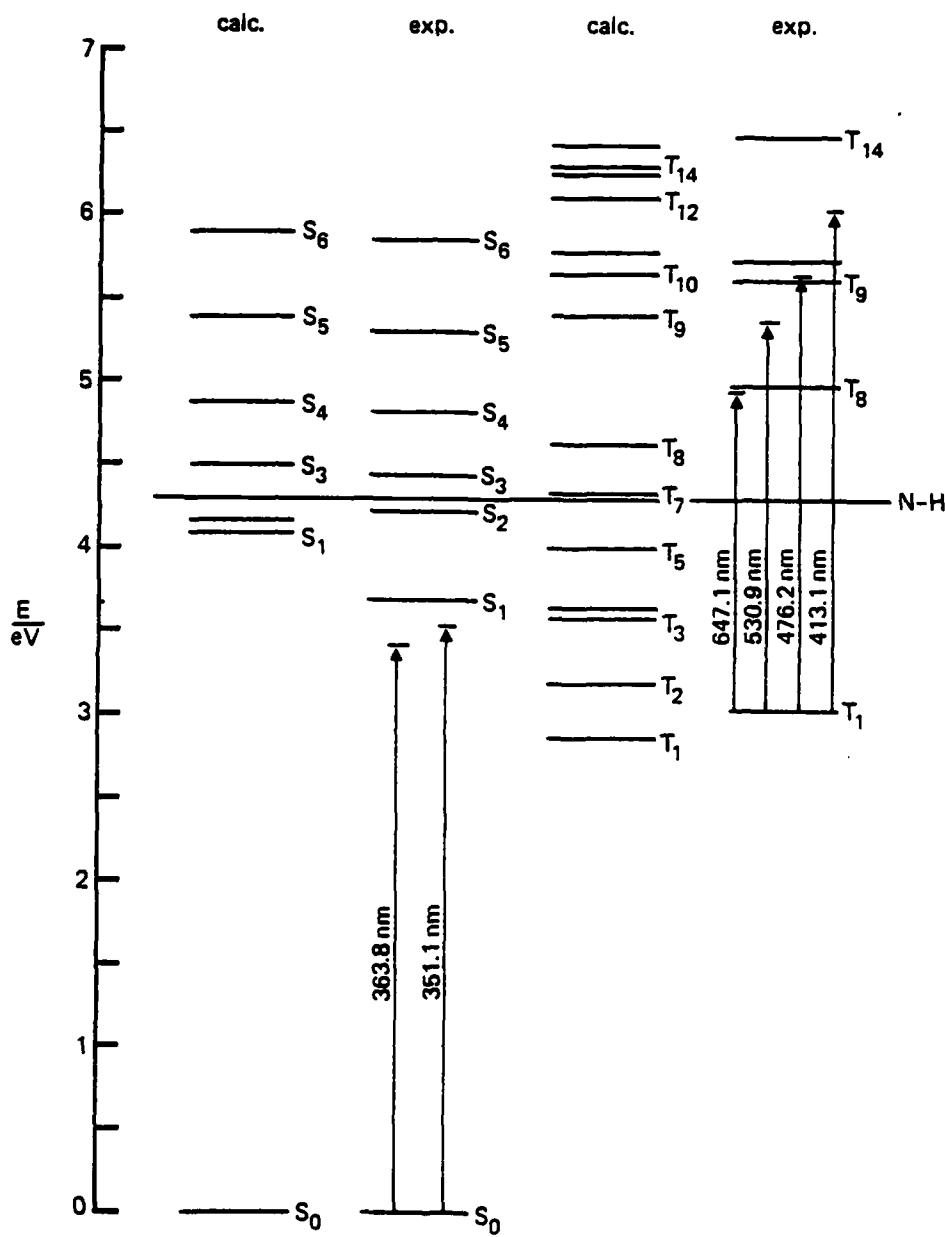


Figure 1. Energy level diagram of carbazole based on data of Refs. 12 and 13, including the N-H bond energy¹⁴ and the photon energies used in our experiments.

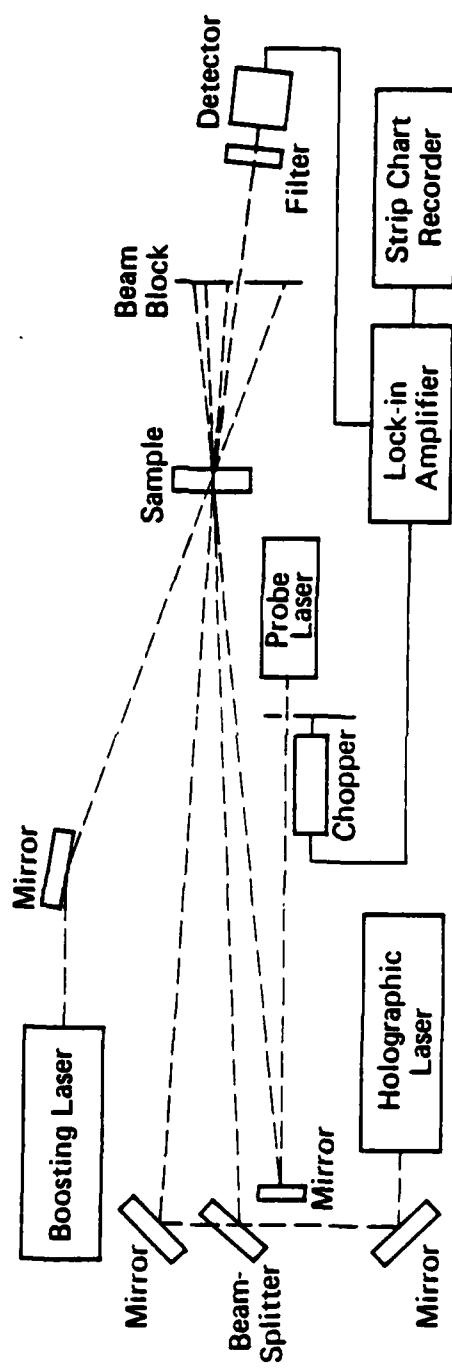


Figure 2. Experimental setup.

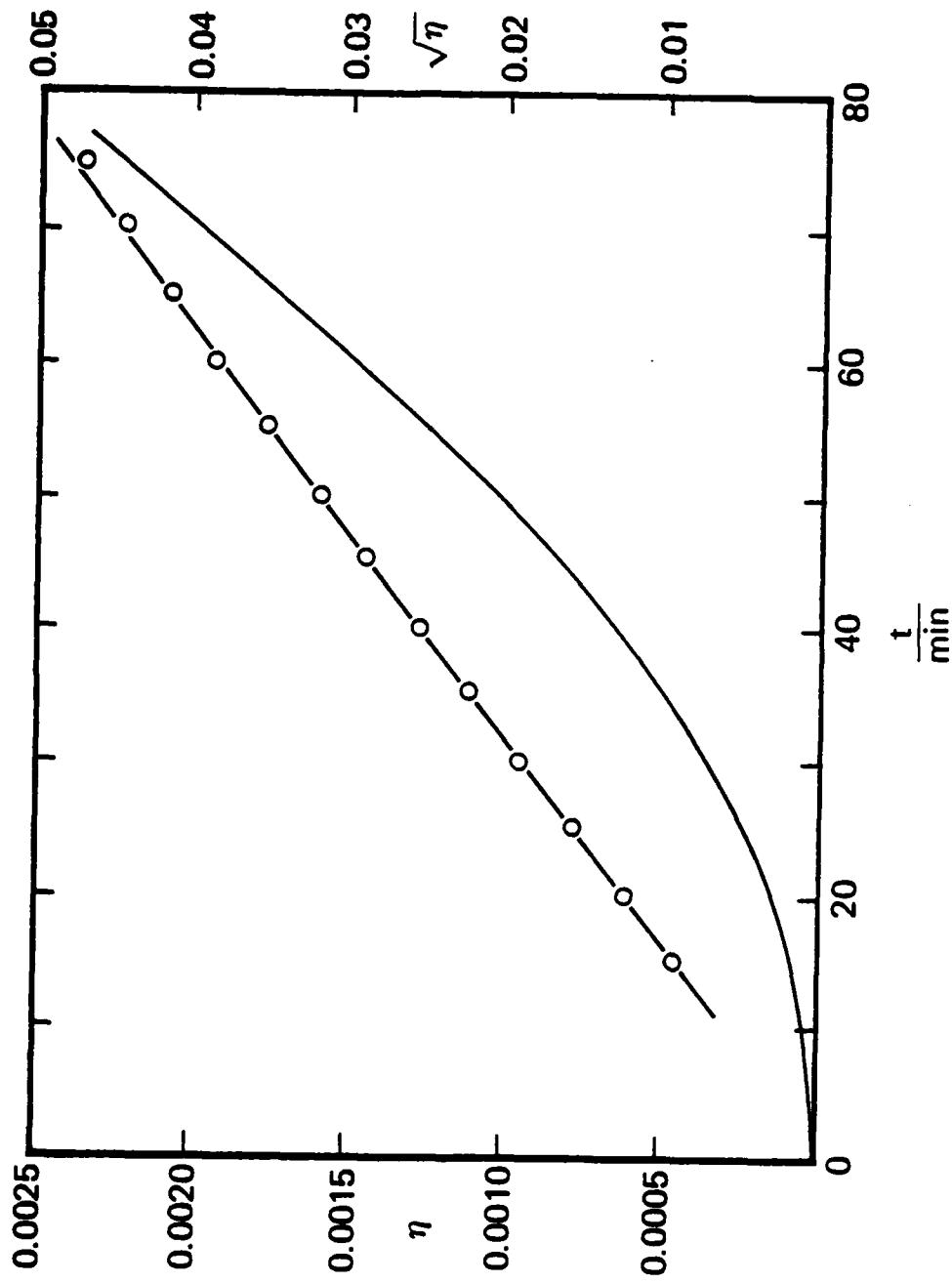


Figure 3. Growth curve of histogram efficiency (solid line) and plot of $\sqrt{\eta}$ vs. time (points).

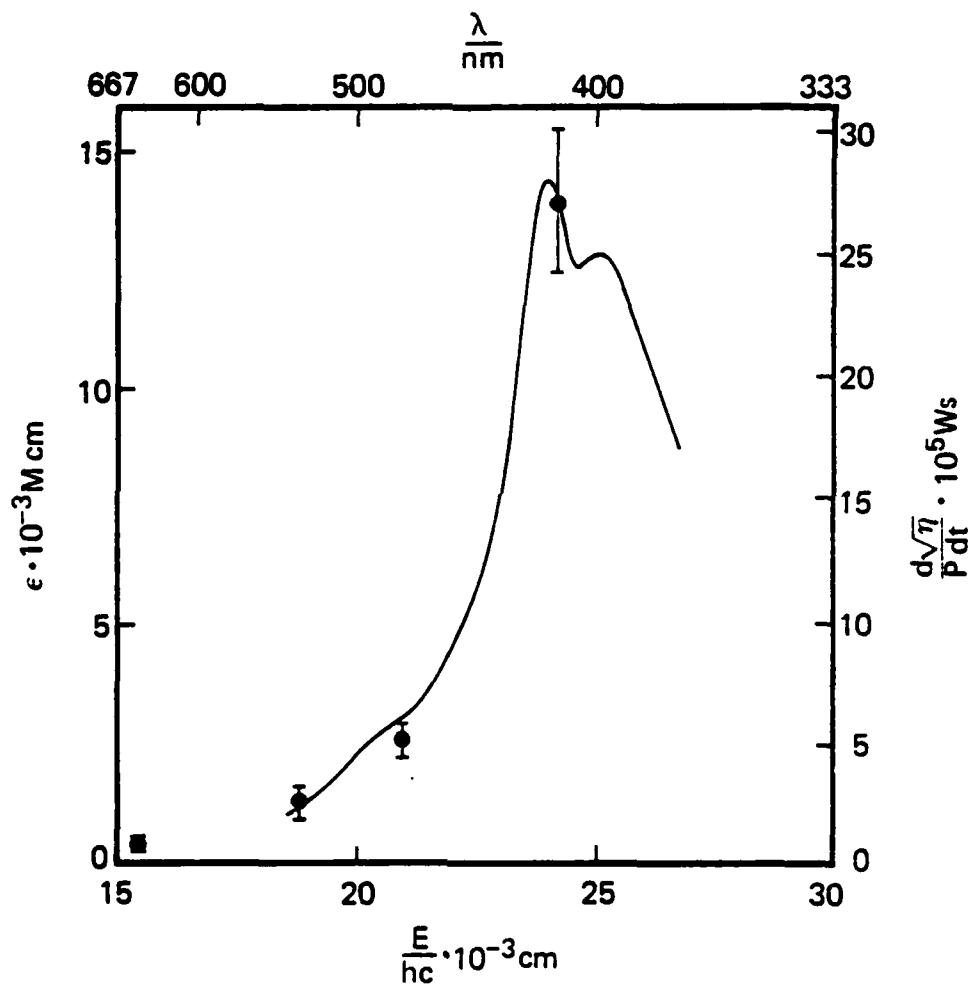


Figure 4. Triplet-triplet absorption spectrum of carbazole (from Ref. 8; solid line) and holographic action spectrum of the second-photon step (points; normalized at 413.1 nm).

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